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Synthesis of perovskite-type $SrTiO_3$ nanoparticles for sensitive electrochemical biosensing applications

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ABSTRACT

In this work, $SrTiO_3$ nanoparticles ($SrTiO_3$NPs), a novel and effective perovskite-type material, are synthesized to modify electrode for the development of sensitive enzymatic electrochemical biosensor applications. The electrochemical behavior of glucose oxidase (GOx) immobilized on $SrTiO_3$NPs-modified glassy carbon electrode is investigated. Scanning electron microscopy and cyclic voltammetry are used to characterize the morphology and assay property of different modified electrodes. Results illustrate that $SrTiO_3$NPs possess large surface area and apparently enhance the direct electron transfer between GOx and modified electrode. The $SrTiO_3$NPs-based enzyme biosensor shows a high sensitivity of 15.6 $mA{\cdot}M^{-1}{\cdot}cm^{-2}$, wide linear range from 0.01 mM to 1.2 mM, and a low detection limit of 3 μM (S/N = 3). Furthermore, the resultant glucose biosensor has excellent selectivity, acceptable repeatability, practicality and stability. The perovskite $SrTiO_3$NPs provide a very attractive and potential electrode material to develop electrochemical biosensors.

1. Introduction

Perovskite structured materials and their derivatives have gained tremendous interest in scientific research and potential technical applications because of their several physical properties [1,2]. Great efforts have been devoted to the synthesis and study of titanate materials such as $ATiO_3$ (A = Ca, Sr, Ba, Pb) [3,4]. Strontium titanate ($SrTiO_3$), an important perovskite material which has a large band gap 3.2 eV [5], has become a very practical electronic material with unique physical and chemical properties [6] due to the nature of the chemical bond between Sr^{2+}, Ti^{4+} and O^{2-} ions in $SrTiO_3$. It therefore has been widely applied in various fields such as gas sensors [7], solar cells [8], UV detectors [9], capacitors [10], and photocatalyst [11]. Since Hu et al. reported very early the synthesis of nanoplated bismuth titanate sub-microspheres and their derivatives for immobilization of protein and electrochemical biosensing [12], there have been very few studies on the application of perovskite materials in biosensing fields [13]. To the best of our knowledge, perovskite $SrTiO_3$ nanomaterials have been not extended to the biosensing applications.

The fast and effective glucose detection is of practical significance in the diagnosis and treatment of diabetes [14]. In the past few decades, great attention has been focused on the development of the third generation glucose biosensor based on direct electron transfer (DET) between glucose oxidase (GOx) and the electrode surface [15]. However, it is difficult to achieve the DET of GOx because the active site of GOx (flavin-adenine dinucleotide, FAD) is limited by the protein shell [16]. It has been found that the nanostructured material-modified electrodes can accelerate the DET due to its electron mediated function [17]. During the past decades, carbon nanomaterials [18,19], metal nanoparticles [20] and semiconductor nanomaterials [21] have been used to accelerate the DET of GOx molecules immobilized on the surface of the electrode. It is still necessary for researchers to search novel type of nanomaterials to develop low-cost and efficient DET-based electrochemical glucose biosensors.

In this work, perovskite-type $SrTiO_3$ nanoparticles ($SrTiO_3$NPs) were simply synthesized and utilized as a novel electrode material to the immobilize GOx. An efficient glucose biosensor on the basis of DET of GOx on $SrTiO_3$NPs-modified electrode was for the first time developed for sensitive determination of glucose. $SrTiO_3$NPs have large surface area and offer a favorable microenvironment to keep biological activity of the immobilized enzyme and to promote fast DET between GOx molecules and electrode surface. Therefore, perovskite-type $SrTiO_3$NPs provide a new-type and prospective matrix for the development of efficient electrochemical biosensors.

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2. Materials and methods

2.1. Materials and reagents

Glucose oxidase (108 U·mg^{-1}, from *Aspergillus niger*) was supplied by Amresco (www.amresco-inc.com). Glucose and chitosan were provided by Sigma-Aldrich (www.sigma-aldrich.com). SrO_2 powders were spontaneously produced by the precipitation reaction of $Sr(NO_3)_2$ and H_2O_2 in ammonia (pH = 8.0) at room temperature. TiO_2 nanocrystals were purchased from Shanghai Academe of Fine Chemicals. D-glucose stock solution is allowed to rotate for 24 h at room temperature before measurement. The electrolyte is phosphate buffer (PBS) obtained by mixing 0.1 M Na_2HPO_4 with 0.1 M NaH_2PO_4 solution. All other chemicals or reagents were treated with the deionized water.

2.2. Apparatus

Cyclic voltammetry and amperometric experiments were investigated in 10.0 mL of phosphate buffer using a CHI 852C electrochemical workstation (Shanghai Chenhua Co. Ltd, China). All performance measurements were performed with a three-electrode system, including a modified glassy carbon electrode (GCE, as working electrode), a saturated calomel electrode (SCE, as reference electrode), and a platinum sheet serving (as auxiliary electrode). Solution pH measurements were carried out using an S-25 digital pH-meter with a glass combination electrode. Scanning electron micrographs (SEM) used to characterize modified electrodes was obtained by a scanning electron microscope (Hitachi S-4800, Japan) at an acceleration voltage of 15 kV.

2.3. The preparation of perovskite-type $SrTiO_3$NPs

$SrTiO_3$NPs were synthesized according to our previously described method [22]. In brief, 0.5982 g SrO_2, 0.3994 g TiO_2, and 1.5 g mixture of KCl and NaCl (molar ratio of 1:1) were mixed and homogenously ground in a carnelian mortar, then transferred into a corundum crucible. The crucible was heated in a Muffle furnace from room temperature to 700 °C for 10 h, and then allowed to cool to ambient temperature naturally. The solid residue was rinsed thoroughly with 1.0 M HNO_3 aqueous solution and deionized water to remove the impurities, and finally dried at 80 °C in air. The white powders were collected directly for the characterization and experiment.

2.4. The preparation of enzyme biosensor

Firstly, the GCE was treated using 0.3 and 0.05 μm alumina slurry (Buhler), and then washed three times with deionized water and ethanol, respectively. The clean GCE was dried by a high-purity nitrogen stream. To accomplish the preparation of enzyme electrode, 3.0 mg of $SrTiO_3$NPs were firstly dispersed in 1.0 mL of 0.5% chitosan solution with sonication. Secondly, 10 mg of GOx was added into 1.0 mL of $SrTiO_3$NPs-chitosan suspension with a slow stirring at for 15 min. Afterwards, 5.0 μL of final suspension was modified on the pretreated GCE surface, and placed in a drier for drying. After the GOx/$SrTiO_3$NPs-chitosan/GCE was rinsed with deionized water to remove the loosely absorbed GOx molecules, the resultant enzyme biosensor was kept at 4 °C in a refrigerator.

3. Results and discussion

3.1. Characterizations of the synthesized $SrTiO_3$NPs, $SrTiO_3$NPs-chitosan, and GOx/$SrTiO_3$NPs-chitosan

Scanning electron microscopy was employed to investigate the surface morphology of different modified electrodes (shown in Fig. 1). The SEM image (Fig. 1a) of $SrTiO_3$NPs displays that the product is mainly composed of polygonal particles with size of 40–150 nm. It can be seen from the SEM image of $SrTiO_3$NPs-chitosan (Fig. 1b), $SrTiO_3$NPs are uniformly dispersed in chitosan to form a stable composite film. This composite film offers a friendly microenvironment for the immobilization of enzyme molecules and promoting the DET process. After GOx molecules are immobilized into the $SrTiO_3$NPs-chitosan film, the morphology of GOx/$SrTiO_3$NPs- chitosan (Fig. 1c) is greatly different from that of $SrTiO_3$NPs-chitosan film, and the molecule aggregation of enzymes are also observed clearly.

3.2. Direct electrochemistry of GOx/$SrTiO_3$NPs-chitosan/GCE

To test the performance of DET of GOx on $SrTiO_3$NPs-chitosan/GCE, cyclic voltammograms (CVs) of $SrTiO_3$NPs-chitosan/GCE, GOx/chitosan/GCE, and GOx/$SrTiO_3$NPs-chitosan/GCE in 0.1 M N_2-saturated pH 7.0 phosphate buffer (scan rate: 100 mV·s^{-1}) were examined in Fig. 2. The CV curve of $SrTiO_3$NPs-chitosan/GCE shows no peaks, indicating no electrochemical redox process in the absence of enzymes. Though a pair of redox peak was observed at GOx/chitosan/GCE, the current response is relatively weak. This is because that oxidized FAD of the GOx molecule is deeply located in the cavity of enzymes, which makes it difficult to transfer electrons to the electrode surface (shown in Eq. (1)). Compared to the GOx/chitosan/GCE, a pair of significant and well-defined redox peaks from FAD and $FADH_2$ of GOx at − 0.443 V and − 0.491 V were obtained from the electrode modified with GOx/$SrTiO_3$NPs-chitosan. Additionally, the reduced peak current of GOx/$SrTiO_3$NPs-chitosan/GCE is 3.0 times larger than that of GOx/chitosan/GCE. This result indicates that $SrTiO_3$NPs can effectively promote the direct electrochemistry of between the GOx active site and the electrode surface. The large current response may results from the larger specific surface area of $SrTiO_3$NPs.

$$GOx(FAD) + 2e^- + 2H^+ \leftrightarrow GOx(FADH_2) \quad (1)$$

The electrochemical behavior of GOx/$SrTiO_3$NPs-chitosan-modified electrode at different scan rates was conducted in Fig. S1A. As seen over a scan rate ranging from 10 to 400 mV·s^{-1}, both of anodic peak current (I_{pa}) and cathodic peak current (I_{pc}) gradually increased, and but the potential of redox peaks shows no obvious shift with increasing scan rate. Moreover, the currents of anodic and cathodic peak display linear response to the scan rate (inset a of Fig. S1A, linear regression equations: I_{pc} = − 0.5662–0.0093v, R^2 = 0.9914, I_{pa} = 0.1147 + 0.0078v, R^2 = 0.9874). The ratio *of* I_{pa}/I_{pc} is close to 1, which indicates that the direct electrochemistry of GOx on $SrTiO_3$NPs-chitosan modified GCE is a quasi-reversible surface-controlled process [23]. Meanwhile, the logarithm of reduction peak current versus the logarithm of scan rate displays a linear relationship (see inset b of Fig. S1A, linear regression equation is $LogI_{pc}$ = − 1.8267 + 0.8940logv, R^2 = 0.9960), and this slope value is close to the ideal slope of the thin-layer electrochemical behavior [24]. According to the Laviron formula [25], the electron transfer rate constant (k_s) for the GOx on $SrTiO_3$NPs-chitosan/GCE is calculated to be 2.4 s^{-1}. The degree of coverage (Γ*) of the GOx molecules on modified electrode surface is measured to be 3.5 × 10^{-11} mol·cm^{-2} from the reduction peak current at 100 mV·s^{-1} according to the formula Γ* = Q/nFA, which is larger than that obtained by other nanomaterial-modified electrodes [20,21,26].

Cyclic voltammetric responses of GOx/$SrTiO_3$NPs-chitosan/GCE have a close association with the pH of the solution. Fig. S1B shows CVs of GOx/$SrTiO_3$NPs-chitosan/GCE in the pH range of 4.0 to 8.0, and the potentials of anodic and cathodic peak both shift negatively with increasing solution pH. The formal potential changes linearly with the solution pH (inset a of Fig. S1B), and the slope of − 48.2 mV·pH^{-1} is close to the theoretical value of − 58.6 mV·pH^{-1} [27]. This indicates that two-proton coupled two-electron transfer participates in the process of redox reaction according to Eq. (1). In addition, the maximum redox peaks current occurs at pH 7.0 (inset b of Fig. S1B), implying the optimal solution pH value for DET of immobilized GOx. To a certain degree, at higher pH value the decreased proton concentration results